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FIRST PRINCIPLES STUDY OF STRUCTURAL, ELECTRONIC AND OPTICAL PROPERTIES OF HALF-HEUSLER ALLOYS LIMGN, NaMGN AND KMGN

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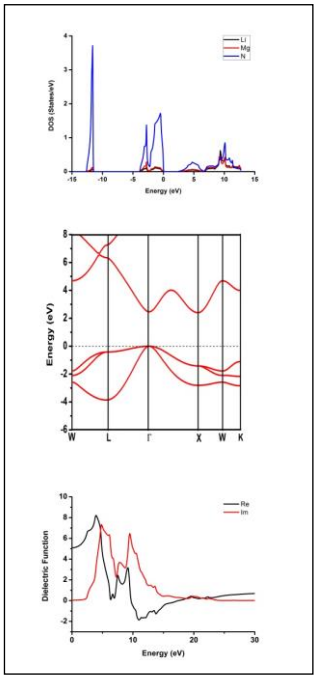
Graphical abstract



Abstract

In this study, we performed our calculations using the full-potential linearized-augmented plane wave (FP-LAPW) method as implemented in the WIEN2k code based on DFT. The generalized gradient functional with the Wu-Cohen (WC) parameterization was used to evaluate the structural, electronic, optical and thermoelectric properties of the materials under this study. We have calculated the structural parameters and our obtained results are in good agreement with available experimental and previous theory calculations. The density of states and band structure figures have been calculated and analyzed. The optical properties that covered by dielectric function, absorption coefficient, refractive index, extinction coefficient, reflectivity and energy-loss function have been calculated and analyzed in a range energy from 0eV to 30eV.

Keywords: Density functional theory, generalized gradient functional, dielectric function, absorption, reflectivity, half-Heusler

Abstrak

Dalam kajian ini, kami telah menjalankan pengiraan dengan menggunakan kaedah potensi penuh gelombang satah linear (FP-LAPW) yang dilaksanakan dalam kod WIEN2K berdasarkan teori berfungsi ketumpatan (DFT). Kecerunan teritlak berfungsi Wu-Cohen (WC) telah digunakan bagi menilai sifat-sifat struktur, elektronik dan optik bahan tersebut. Kami telah membuat pengiraan parameter kekisi dan keputusan yang didapati bersetuju dengan pengiraan eksperimen dan teori yang sebelumnya. Gambar-gambar ketumpatan keadaan dan struktur jalur adalah yang telah dikira dan dianalisis. Ciri-ciri optik seperti fungsi dielektrik, pekali penyerapan, indeks pembiasan, pekali pemupusan, pemantulan dan fungsi kehilangan tenaga telah dikira dan dianalisis dalam julat tenaga daripada 0eV sehingga 30eV.

Kata kunci: Teori berfungsi ketumpatan, kecerunan teritlak, fungsi dielektrik, penyerapan, pemantulan, separuh Heusler

1.0 INTRODUCTION

Presently Half-Heusler alloys are known as the best materials for different applications such as optoelectronics, electrical, thermoelectric and piezoelectric applications etc. Half-Heusler alloys possess high spin polarization, exhibit half-metallic property, and sustain aggressive environment [1-3]. They are established from the combination of a rock-salt with a zinc blende type structure by a general formula XYZ. Where X represents the most electropositive element, Y is intermediate electropositive and electronegative element while Z is the most electronegative element. The

combination of different elements can provide a wide range of electronic states and physical properties. LiMgN, NaMgN and KMgN belongs to half-Heusler structure family. Therefore, these materials are also considered as potential materials for certain applications. However to venture these materials further for future technologies, more studies related to their structural, electronic and optoelectronic properties are necessitated. In this paper, we have been adopted density functional theory (DFT) in order to investigate physical properties of LiMgN NaMgN and KMgN half-Heusler alloys.

2.0 COMPUTATIONAL DETAILS

In this study, we performed our calculations using the full-potential linear-augmented plane wave (FP-LAPW) method [4] as implemented in the WIEN2k code [5] based on DFT. The generalized gradient functional with the Wu-Cohen (WC) parameterization [6] was used to evaluate the structural, electronic and optical properties of the materials. This exchange correlation functional was chosen because this functional is considered to be simple and more accurate for solids [6]. The value of RMTKMAX = 9 was chosen in the irreducible wedge of the Brillion zone, where RMT is coincide as a minimum of the muffin tin radii of the atoms and KMAX correspond to the plane-wave cut off. The total energy convergence criteria for self-consistent field (SCF) were set to 10^{-5} eV. In our calculations, the radius of muffin tin sphere for Mg, Na and K was set to 1.96 a.u whereas for Li and N to 1.77 and 1.87 a.u respectively. An 18x18x18 k-mesh was applied in the irreducible Brillouin zone for optimizing the lattice parameters of structures whereas the electronic and optical properties were calculated along 34x34x34 k-mesh which relatively generates 1059 k-points.

3.0 RESULTS AND DISCUSSION

3.1 Structural Properties

The structural properties of LiMgN, NaMgN and KMgN were calculated using GGA-WC schemes to evaluate the exchange correlation energy. Figure 1 shows the successfully generated crystal structure of materials. The structures are called as half-Heusler structure with space group F43m (space gr. No. 216). The Wyckoff positions for Li, Na and K are (0.5, 0.5, 0.5) while Mg at position (0, 0, 0) and N at (0.25, 0.25, 0.25). Simulated unit cells were optimized in order to determine the structural parameters of materials. The calculated total energies are fitted to the Murnaghan equation of states (EOS) [7].

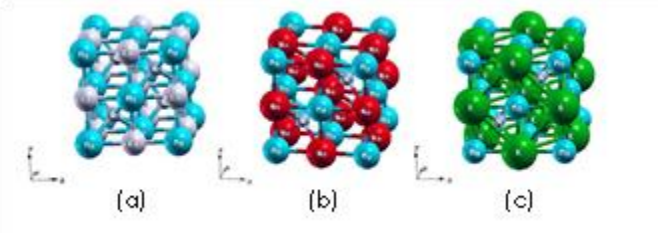


Figure 1 The optimized crystal structure of (a) LiMgN, (b) NaMgN and (c) KMgN

The results are shown in Figure 2, and then the calculated lattice constant (a), bulk modulus (B) and its pressure derivative (B') are listed in Table 1. From the results, it can be seen that our calculated results are in close agreement with previous work. Calculations show that calculated lattice constant for LiMgN is in good agreement to the experiment and other theoretical work whereas results for NaMgN and KMgN are also agree with previous calculations.

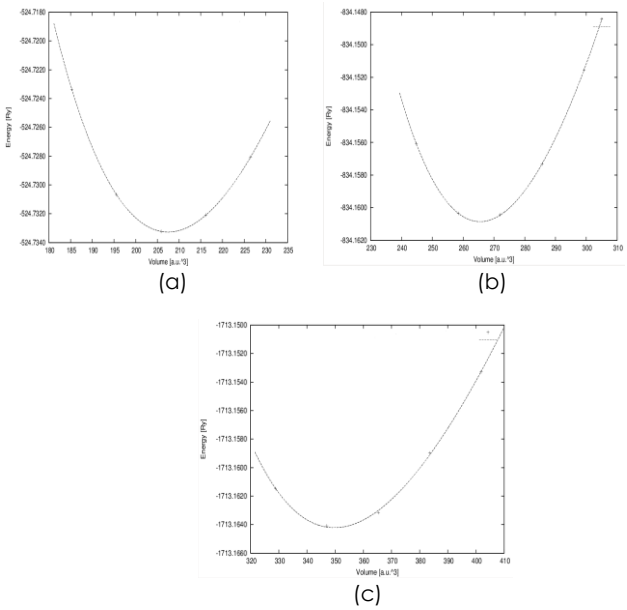


Figure 2 Variation of total energy as a function of volume for (a) LiMgN, (b) NaMgN and (c) KMgN

Table 1 Calculated lattice parameter (a), bulk modulus(B) and its pressure derivative B along with experimental and theoretical work

Materials	LiMgN	NaMgN	KMgN
a (Å)	4.97	5.40	5.92
B (GPa)	101.4826	76.7056	56.2324
B	3.9839	3.6566	5.8631
Experiment	4.96[8]	-	-
Other theoretical work	5.01[9]	5.45[10]	6.01[11]

3.2 Electronic Properties

In order to study the electronic and optical properties of these materials, we need to have knowledge about their electron density of states (DOS). The same parameterization was used to calculate the DOS of the materials and the outcomes are shown in Figure 3.

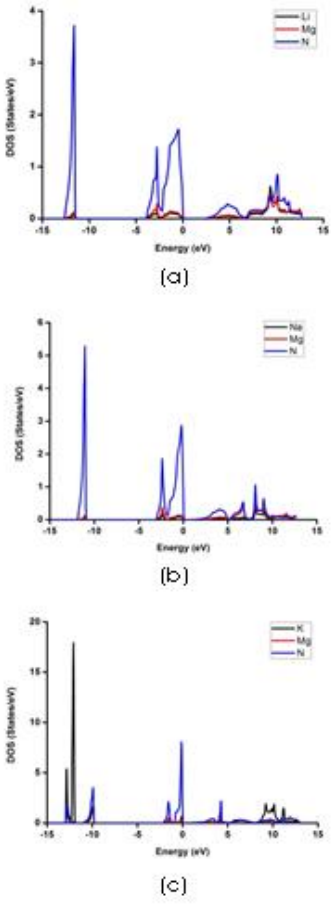


Figure 3 The total DOS (States/eV) of (a) LiMgN, (b) NaMgN and (c) KMgN

Based on the figures for LiMgN and NaMgN, the valence band maximum (VBM) are mainly composed by atom N and the projected DOS (Figure 4) are arising from the p orbital of N. Whereas, for conduction band minimum (CBM) are mainly built up from s and p orbitals of Mg and p orbital of N atoms ahead with a small contribution from s orbitals of atom Li and Na. Hence, the states in VBM are strongly contributed by N atoms whereas the CBM are mainly by Mg and a little bit by Li and Na atoms. However, DOS of KMgN are different as compared to DOS of LiMgN and NaMgN. The results showed the dominant states at VBM near to Fermi level that come from N while at deep VBM come from K atoms. The same situation happened at CBM. Therefore, it is clear from this result that the states in VBM and CBM are mainly from N atoms near to Fermi level and K atoms states are at deep part of CBM and VBM.

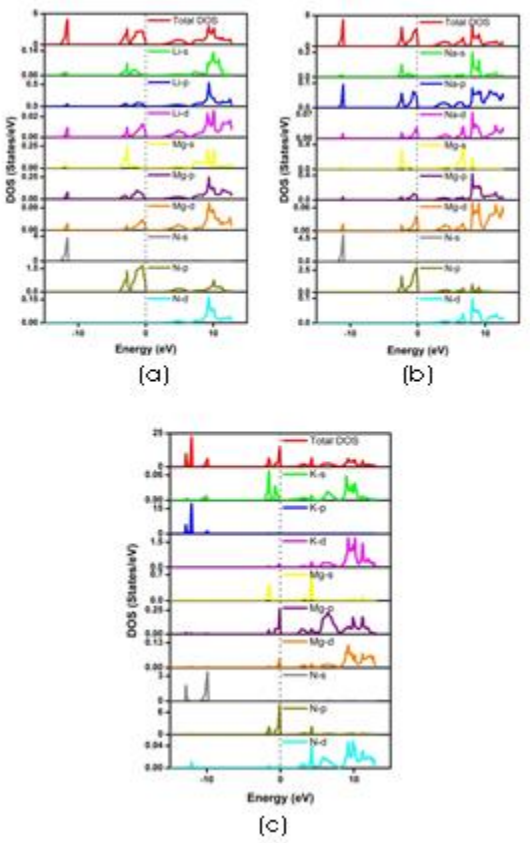


Figure 4 The total and partial DOS (States/eV) of (a) LiMgN, (b) NaMgN and (c) KMgN

The band structure calculations have been shown in Figure 5. LiMgN and NaMgN are direct band gap materials at Γ symmetry point having band gap energy values 2.4 eV and 0.78 eV respectively. For KMgN, the calculations give an indirect band gap which is at Γ symmetry point at minimum conduction band and X point at maximum valence band with the estimated band gap energy is 0.12 eV. All these results were in good agreement with that of the previous work [9].

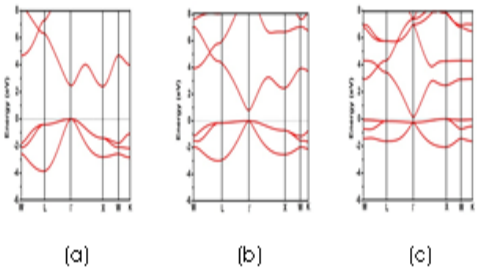


Figure 5 Band structures of (a) LiMgN, (b) NaMgN and (c) KMgN

3.3 Optical Properties

The optical properties can be obtained by determination of dielectric function. The complex dielectric function, $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$ were computed first. ε_1 represents as the real part while ε_2 represents as the imaginary part, and both of these describe the propagation properties and optical absorption in a medium respectively. This function is mainly describing the electrical and optical properties of materials. Kramer-Kronig relation was used to calculate the real part $\varepsilon_1(\omega)$ where $\varepsilon_1(\omega)$ was obtained from the imaginary part of dielectric function $\varepsilon_2(\omega)$. While the imaginary part $\varepsilon_2(\omega)$ can be calculated from the momentum matrix elements between the occupied states in valence band and unoccupied states wave functions in the conduction band.

The optical parameters that we are focusing in this work, are dielectric function, absorption coefficient, $\alpha(\omega)$, energy loss spectrum, $L(\omega)$ reflectivity, $R(\omega)$ and refractive coefficient that can be obtained from $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$. All the results have been presented in Figure 6-10 and all these parameters were investigated in the energy range 0–30 eV. Figure 6 shows the dielectric function of LiMgN, NaMgN and KMgN. The calculated values for the real part, $\varepsilon_1(\omega)$ of dielectric function at 0eV for LiMgN, NaMgN and KMgN are 5.0925, 6.70779 and 8.9753 respectively. These values would determine the capability of the materials to be as an electron acceptor. It shows that KMgN has great potential to be the electron acceptor compared to LiMgN.

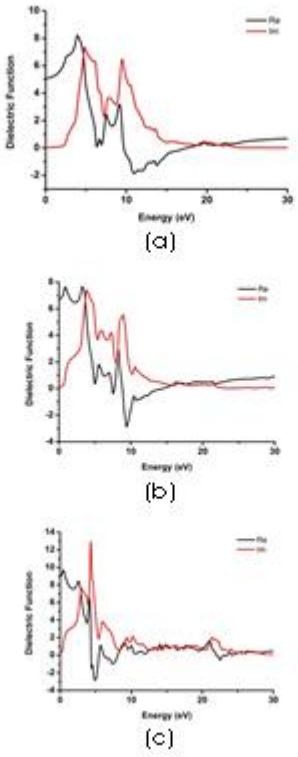


Figure 6 Dielectric function of (a) LiMgN, (b) NaMgN and (c) KMgN

The absorption spectra, $\alpha(\omega)$ of the materials have been shown in Figure 7. This parameter provide describe the potential of materials to capture incident light. From the figure, the maximum peaks absorption found in LiMgN, NaMgN and KMgN are 190.20, 183.33 and 223.523 respectively. Hence this shows KMgN has the greater capability in absorbing light.

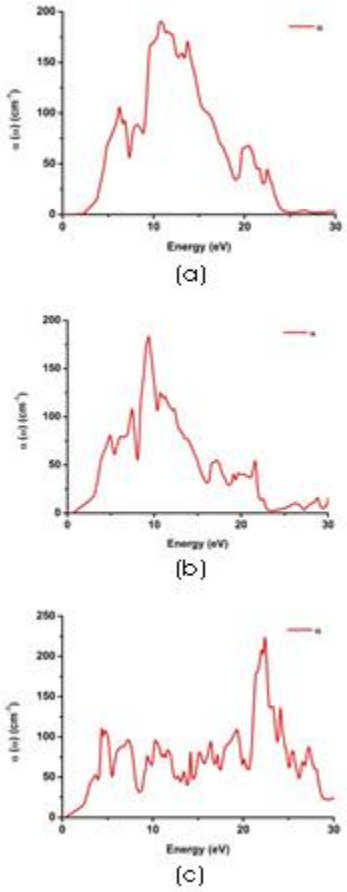


Figure 7 Absorption spectra, $\alpha(\omega)$ of (a) LiMgN, (b) NaMgN and (c) KMgN

Figure 8 shows the energy loss function $L(\omega)$ of LiMgN, NaMgN and KMgN alloys. This parameter describes the energy loss when an electron passing through a medium. From the results, it is clearly shows that LiMgN and NaMgN have weak energy loss under 10eV and experienced an abrupt increased when energy above 10eV. While for KMgN, the highest loss function occurs at energy 24.59eV. However, KMgN has the smallest loss energy which is in contradiction to LiMgN. The reflectivity spectra, $R(\omega)$ of the alloys are shown in Figure 9. These graphs show a variable pattern at range energy from 0eV to 30eV and start to reach plateau after 30eV. The maximum reflectivity for LiMgN and NaMgN are almost similar which is about 0.55 while for KMgN is

0.48. Our calculations indicated that the level of transparency of KMgN is higher than others.

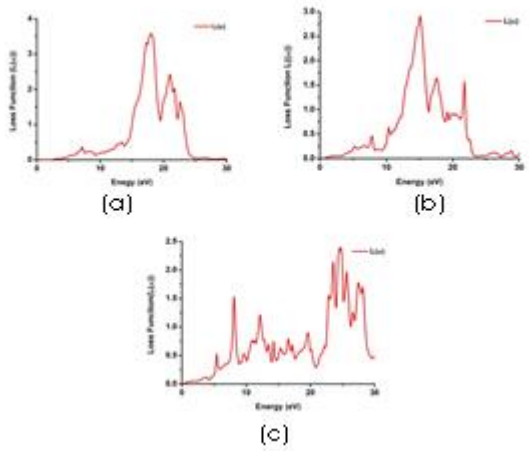


Figure 8 Loss function, L(ω) of (a) LiMgN, (b) NaMgN and (c) KMgN

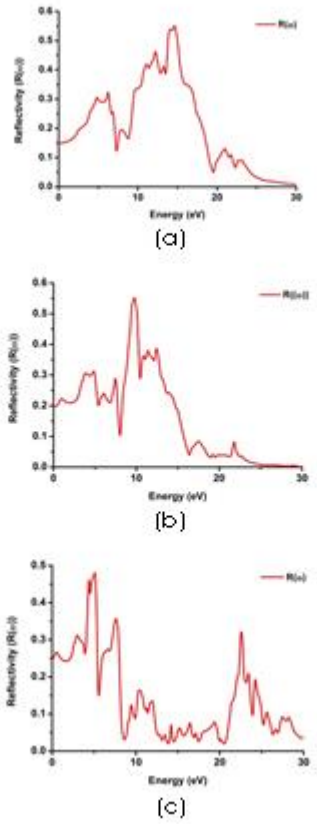


Figure 9 Reflectivity, R(ω) of (a) LiMgN, (b) NaMgN and (c) KMgN

Figure 10 shows the refractive index and extinction coefficient of materials. The refractive index for all alloys showed a similar pattern with different level of indices. The highest values of refractive index at 0eV for LiMgN, NaMgN and KMgN are 2.3, 2.6 and 3.0 respectively. This shows that KMgN has higher tendency to refract photon compared to others. For extinction coefficient, LiMgN, NaMgN and KMgN are having maximum intensity of 1.75 at 10.68eV, 1.94 at 9.32eV and 2.49 at 4.37eV respectively.

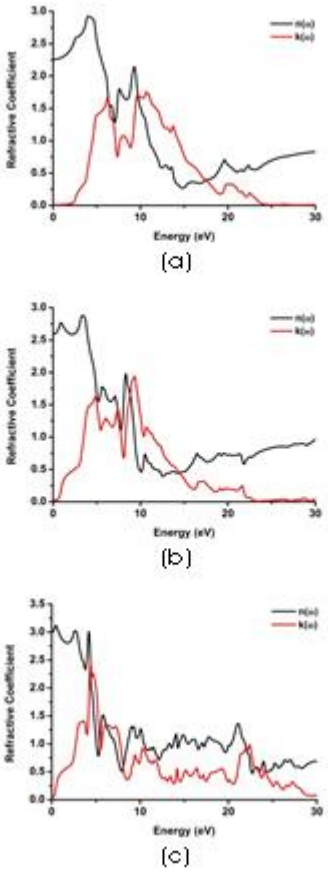


Figure 10 Refractive coefficient of (a) LiMgN, (b) NaMgN and (c) KMgN

4.0 CONCLUSION

The structural, electronic and optical properties of half-Heusler alloys LiMgN, NaMgN and KMgN were computed using full-potential linear-augmented plane wave (FP-LAPW) method formed within DFT. Generalized gradient approximation with the Wu-Cohen (WC) parameterization was used to calculate the exchange correlation energy and potential. We have compared our results with the already done experimental and theoretical works. Our results are matching with the previous calculations with different exchange correlation approximations. Thus, the DFT approaches show its ability to solve the complex equation in more easy way.

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